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Electronic transport through carbon nanotubes – effect of contacts, topological defects, dopants and chemisorbed impurities

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ABSTRACT

Electronics based on carbon nanotubes (CNT) has received a lot of attention recently because of its tremendous application potential, such as active components and interconnects in nanochips, nanoelectromechanical systems (NEMS), display devices, and chemical and biological sensors. However, as with most nanoelectronic systems, successful commercial deployment implies structural control at the molecular level. To this end, it is clearly necessary to understand the effect of contacts, topological defects, dopants, and chemisorbed atoms and molecules on the electronic transport through CNT's. This paper summarizes our computational efforts to address some of the above questions. Examples include: wetting properties and bonding strength of metal contacts on the CNT surface, the effect of Stone-Wales defects on the chemisorption of O_2 and NH_3, and how such chemisorbed species and defects effect the electronic transmission and conductance. Our approach is based on first-principles density functional theory (DFT) to compute equilibrium structures, and non-equilibrium Green's function (NEGF) methods, using both DFT and semi-empirical tight-binding formalisms, for computing electronic transport properties.

Keywords: Nanotubes, Electronic Transport, DFT, NEGF.

1 INTRODUCTION

CNTs have been a popular area of research for more than a decade because of the promise of a host of commercial applications, including: Field Emission-based Flat Panel displays, novel semiconducting devices in microelectronics, hydrogen storage device, structural reinforcement agents, chemical sensors, and ultra-sensitive electromechanical sensors. However, for many applications, especially involving electronics and sensors, the device performance and commercial success could hinge on our ability to control structural integrity at the molecular level. This is where molecular modeling could play a crucial role in assessing and isolating various effects, and provide useful guidance to experimental fabrication. Previously we have used molecular modeling to investigate CNT-based field-emission devices and nano-electromechanical sensors (NEMS) [[1]]. In this work, we focus more on CNT-metal contacts and the use of CNTs in chemical sensors.

2 CNT-METAL CONTACTS

Sensing operations are usually associated with a change in the electrical response of the active component of the sensing device. For CNT-based sensors, the measured conductance depends strongly on the contact resistance of metal-CNT junctions at the two ends. Besides, carbon nanotubes interacting with metal nanoparticles are gaining considerable interest as sensing materials, catalysts, in the synthesis of metallic nanowires, as well as in nanoelectronics applications as Field-Effect-Transistor (FET) devices. A systematic study of electron-beam-evaporation-coating of suspended SWNT with various metals reveals that the nature of the coating can vary significantly depending upon the metal [[2]]. Thus, Ti, Ni and Pd form continuous and quasi-continuous coating, while Au, Al and Fe form only discrete particles on the SWNT surface. In fact, Pd is a unique metal in that it consistently yields ohmic contacts to metallic nanotubes [[3]], and zero or even negative Schottky barrier at junctions [[4]] with semiconducting SWNTs for FET applications. The Schottky barrier (for p-channel conductance) could, in principle, be made even lower if a higher work function metal, e.g., Pt is used. Unfortunately, Pt appears to form non-ohmic contacts to both metallic and semiconducting SWNTs with lower p-channel conductance than Pd-contacted junctions.

The computed interaction energy of a single metal atom on a SWNT [[5]] follows the trend Eb(Ti) » Eb(Pt) > Eb(Pd) > Eb(Au). These trends would suggest that Ti sticks the best to the SWNT and Au the worst, in good agreement with experiment. However, it does not explain why Pt consistently makes worse contacts than Pd, and why Ti, in

spite of its good wetting of a CNT surface, yields Ohmic contacts only rarely [[3]]. A detailed investigation of the metal-SWNT contact at full atomistic detail is a significant undertaking, and is likely beyond the realm of today's first-principles Quantum Mechanics codes. Nevertheless, as a first attempt, it is instructive to look into the interactions of SWNTs with metallic entities beyond single atoms.

To this end, we carried out binding energy calculations of metallic monolayers, multilayers, and 13-atom clusters with a sheet of graphite, which is a representative of wide-diameter CNTs. In addition, the interaction of a semiconducting (8, 0) tube with flat metallic surfaces was also studied. Three metals were considered for concreteness – Au, Pt, and Pd. Calculations were performed with the DFT code DMol^3 [[6]] under periodic boundary conditions using the same settings as in section III. Details are given in ref. [[7]]. We only summarize the main results below:

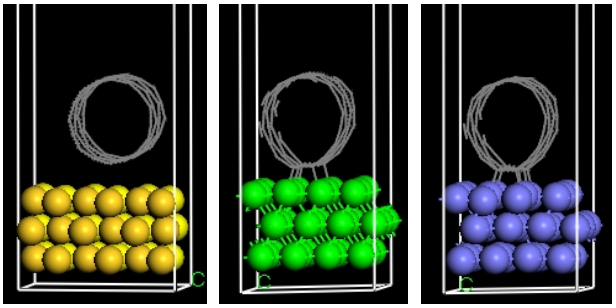
i) For isolated Au, Pd, and Pt atoms on a sheet of graphene, the respective binding energies are 0.30, 0.94 and 1.65 eV respectively, i.e., in the same order as previous computed values on a (8, 0) Single-walled nanotube (SWNT) [[5]]. The binding sites are also quite similar, although the binding energies to graphene are ~ 40% smaller than to the SWNT, whose finite curvature imparts higher reactivity.

ii) For monolayer or multilayer of metal atoms on graphene, most of the metal binding arises from metal-metal interaction rather than metal-graphene interaction. This is due to high cohesive energies of the metals in the bulk crystalline state. If only the metal-graphene part of the interaction is considered, the binding for Pt falls rapidly with layer thickness, and is less than that of Pd for 3-layer films, perhaps indicating possible instability of Pt films beyond a certain thickness. This is likely due to much higher cohesive energy of Pt as compared to Pd. For Au, isolated atoms as well as films interact very weakly with graphene, in agreement with experimentally observed poor wetting properties.

iii) 13-atom Pd clusters bind more strongly to the graphene surface than a 13-atom Pt cluster. The Pd cluster, in particular, gets significantly distorted from its ideal icosahedral geometry. Spin might play an important role in such binding calculations, and requires a more careful analysis.

iv) We predict a critical cluster size of a few tens of metal atoms below which it should wet a graphene (and therefore nanotube) surface uniformly, and above which non-uniform clustering is likely. Using a simple model we show that the critical cluster size for Pt is smaller than that for Pd, implying higher propensity of Pt to form a non-uniform coating unless it is deposited in the form of ultrafine nanoparticles.

v) Finally, SWNTs placed on flat Pt or Pd surface can form direct covalent bonds to the metal, which, along with the resulting deformation in tube cross-section might alter its electronic properties and impact performance of electronic devices based on such geometry. Interaction with a Au surface is weak, and the SWNT cross-section remains circular. This phenomenon is illustrated in Fig. 1.



(a) (b) (c)

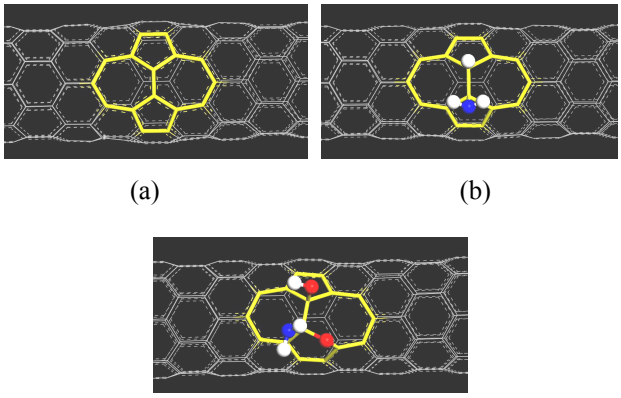
Fig. 1. (8, 0) SWNT on metal surfaces: (a) Au (100); (b) Pd (111); (c) Pt (111). On the Au surface the SWNT is essentially weakly physisorbed. For Pd and Pt surfaces, the metal-adjacent C-atoms undergo $sp^2 \rightarrow sp^3$ transition, which significantly deform the CNT cross-section. Binding on Pd is slightly higher than on Pt.

3 NANOTUBES AS NH_3 SENSORS

Of all the projected application areas of Nanotechnology, gas sensors based on CNTs and nanowires appear to be the ones closest to commercial reality. Detection of gas molecules such as NO_2, O_2, NH_3, N_2, CO_2, H_2, CH_4, CO, or even water is important for monitoring environmental, medical or industrial conditions. Recently, it was reported [[8]-[12]] that the measured electrical conductance of a semiconducting single-walled nanotube (s-SWNT) at room temperature increases by three orders of magnitude upon exposure to 0.2 % of NO_2, and decreases by two orders of magnitude upon exposure to 1% of NH_3. Exposure to O_2 also appears to consistently increase the electrical conductance, although the effect is not as dramatic as for NO_2.

Considering the fact that the s-SWNT used in the experiment of ref. [[8]] was effectively p-type (i.e. holes were the majority carriers), the observed behavior of conductance changes can be rationalized through a simple charge transfer model in which NO_2 molecules accept electrons from the s-SWNT, thus increasing the hole population, while the NH_3 molecules donate electrons, thus depleting the hole population and the conductance. However, such a conclusion for NH_3 is inconsistent with theoretical results [[13], [14]] that NH_3 molecules interact very weakly with pure SWNTs, which would make charge transfer very difficult to explain.

A logical resolution to the above problem would be to note that SWNTs are likely to have some defects incorporated either thermally or during high-temperature growth conditions. Also, they are not in isolation, and surrounding environment (oxygen, water vapor), or the substrate, or metal contacts at the ends might directly or indirectly provide a mechanism of binding of the gas molecules. In the rest of this section we summarize our initial results for chemisorption of NH_3 at various types of topological defects on a (8, 0) s-SWNT. Below we highlight the main conclusions so far, without specific reference to any numbers, which depend on the details of the DMol^3 parameters. Such details will be published elsewhere.



(a) (b)

(c)

Fig. 2. Dissociation of NH_3 at a Stone-Wales (SW) defect on a (8, 0) SWNT: (a) SW defect as is; (b) NH_3 dissociated into NH_2 and H fragments each bonded to a different C-atom; (c) NH_3 dissociation at SW site with a pre-dissociated O_2 molecule, resulting in NH_2 an OH fragments bonded to different C-atoms. C-atoms and C-C bonds in the SW defect are shown in Yellow, O-atoms in Red, N-atom in Blue, and H-atoms in White.

i) Most of the investigations so far have been carried out on 5775 defects of the Stone-Wales (SW) type [[15]] (Fig. 2(a). We are also looking into two other types of defects, i.e., a missing carbon atom or monovacancy (V), and an extra carbon atom in the form of a bridge between two existing carbons, in other words, an interstitial (I). The formation energies were found to be in the order $E_{SW} < E_I < E_V$.

ii) Binding energy of a *physisorbed* NH_3 molecule to a defect-free (8, 0) tube is very small, in agreement with previous calculations. At a SW defect the binding increases somewhat, but not enough to stabilize the molecule at room temperature. In conjunction with weak binding the charge transfer from the physisorbed molecule to the nanotube is very small, which implies negligible effect on electronic transport, and hence the electrical conductance.

iii) It appears that any changes in conductance would appear only for structures in which the NH_3 chemically reacts with the nanotube (see section 4). The simplest reaction one could imagine involves dissociation of NH_3 into NH_2 and H groups, each attaching to different C-atoms of the SWNT. With DMol^3 we have computed activation barriers to such a reaction. For defect-free SWNT it appears that this barrier is prohibitively expensive, and the process is endothermic. At a SW defect, the reaction becomes mildly exothermic, but unfortunately the barrier is still high. The resulting product in shown in Fig. 2(b).

iv) In reality, however, there could be other impurities already pre-adsorbed at the SW site, which could facilitate the dissociation of NH_3. To this end, we have investigated the possibility of the dissociation of an O_2 molecule into two different (two-fold) bridging O-atoms [[16]]. In the presence of this preadsorbed oxygen, NH_3 dissociation becomes a highly exothermic reaction with an energy barrier < 20 kcal/mol, which certainly makes such reaction possible at room temperature. See Fig. 2(c) for an illustration of the resulting product.

Predicting stable chemical structures upon adsorbate dissociation is only one half of the puzzle. In order to truly predict the working of a sensor device, it is necessary to compute electronic transport and the resulting electrical conductance through the nanotube. In section 4 we sketch our plans for such an investigation.

4 EFFECT OF CHEMISORPTION ON ELECTRONIC TRANSPORT

The transport properties of chemisorbed nanotubes are studied using a multi-scale approach involving DFT code DMol^3 [[6]], the density functional based tight binding (DFTB) [[17], [18]] and Green's functions methods. The reason for this multi-scale approach is we are interested in studying transport in long nanotubes with many chemisorbed sites. We start with optimized structures generated using DMol^3, which while being accurate cannot handle a large number of atoms. The DMol^3 calculations are performed on short nanotubes with one or a maximum of two adsorbates. Using these structures as a template, we construct long nanotubes with adsorbates, which form the input to DFTB calculations. DFTB can handle many hundreds of atoms and is hence used to obtain the overlap and Hamiltonian matrices. To gain further confidence in this multi-scale approach, we compared the charge transfer between nanotube and adsorbates, obtained from DFTB with DMol^3, and found quite good agreement.

As the dimension of the overlap and Hamiltonian matrices is in thousands, we exploit the one dimensionality of nanotubes to reconstruct the overlap and Hamiltonian matrices in a banded form by including more than nearest neighbor interaction. The diagonal blocks of this banded matrix typically correspond to a few rings of the underlying nanotube and adsorbates associated with these rings. This

banded matrix is the input to our Green's function code to compute the transmission probability, density of states and charge density [[19]].

The change in current flowing through nanotubes due to gas adsorbtion could be due to a variety of reasons: doping of nanotube bulk, modulation of the Schottky barrier between metal and nanotube, and change in transmission due to defect induced scattering. There have been many studies of the role of doping using DFT calculations on periodic systems and clusters [[20]-[24]]. The role of Schottky barrier modulation due to gases has also been phenomenologically studied [[25], [26]]. Here, we focus on the adsorbate induced change in transmission probability and density of states, and study their dependence on the spatial density of adsorbates. One important aspect of the calculation is modeling of contacts. We currently treat the contacts either as semi-infinite carbon nanotube leads or as a metal with featureless density of states. While such a model will not capture the exact nature of bonding between metal contact and nanotube atoms in experimental situations it is sufficient for study of change in transmission probability as a result of scattering centers induced by adsorbates.

We find that physisorbed adsorbates do not alter the relative eigenvalue distribution and density of states of the carbon nanotube, as expected. As a result, the transmission probability of a bare nanotube is not affected. On the other hand, chemisorbed adsorbates are seen to significantly affect the eigenvalue distribution obtained from DFTB. Results of the change in transmission probability due to the chemisorbed adsorbates described in the previous section will be discussed in the talk.

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